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(54) Oxygen free plasma stripping process

(57) A method for stripping photoresist 16 and/or removing post etch residues from an exposed low k dielectric layer 14 of a semiconductor wafer 98 in the presence or absence of copper. The method comprises creating an oxygen free plasma by subjecting an oxygen free gas to an energy source to generate the plasma having electrically neutral and charged particles. The charged particles are then selectively removed from the

plasma. The electrically neutral particles react with the photoresist 16 and/or post etch residues to form volatile gases which are then removed from the wafer 98 by a gas stream. The oxygen free, plasma gas composition for stripping photoresist 16 and/or post etch residues comprises a hydrogen bearing gas and a fluorine bearing wherein the fluorine bearing gas is less than about 10 percent by volume of the total gas composition.

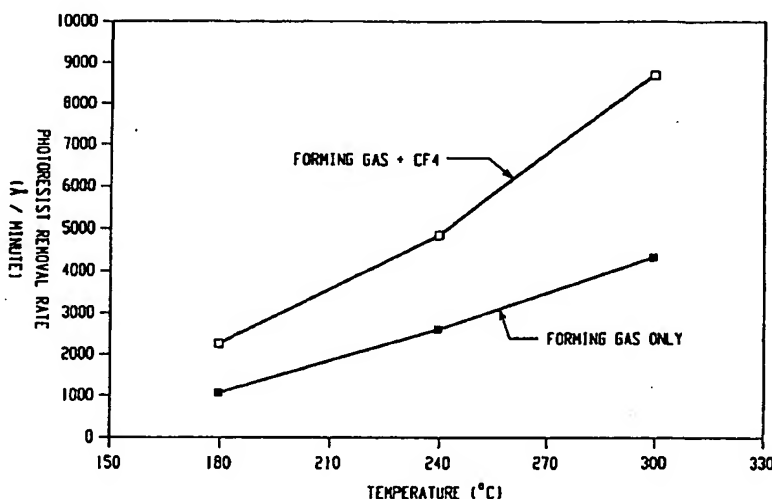


Fig. 5

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vice performance, yield and reliability of the final integrated circuit.

[0008] Copper is a readily oxidizable, ductile material and as such, is prone to oxidation with the use of oxygen containing plasmas. The build-up of copper oxide from exposure to oxygen containing plasmas is detrimental to device performance. Higher contact resistance results which impedes the flow of current through the integrated circuit. Consequently, clock speed and electromigration can be affected.

[0009] Another problem with the use of the oxygen plasma on low k dielectric layers is that the oxygen plasma has been found to change the dielectric constant during ashing. For example, it has been found that doped oxide low k materials, such as nanoglasses and aerogels, exposed to the oxygen containing plasma result in an increase in the dielectric constant. An increase in dielectric constant undesirably affects interconnect capacitance and cross talk. It is believed that this is due to the oxidation of the Si-H and Si-OH bonds to form Si-O bonds. Still further, the use of an oxygen plasma with integrated circuits having copper as the interconnect tends to oxidize the exposed copper surface and deleteriously affect device performance.

[0010] U.S. Patent No. 4,201,579 discloses a method for removing photoresist from a substrate by a hydrogen plasma. The hydrogen plasma removes photoresist from an easily oxidizable metal surface such as gold, silver, copper and the like. The patented process is comparatively slow, not amenable to high throughput processing and not effective for removing most residues from the semiconductor wafer.

[0011] Accordingly, it is an object of this invention to provide a high throughput dry ashing process with high selectivity for removing photoresist and post etch residues from integrated devices having copper interconnects and low k dielectric insulating layers. It is a further object of this invention to provide a process that is non-oxidative such that any exposed copper interconnects are not oxidized during the ashing process. Moreover, it is another aspect of this invention that the novel ashing processes remove any native oxide that may have formed on the exposed copper interconnects, thus improving device performance.

#### Summary of the Invention

[0012] In general, the present invention is directed to a method for stripping photoresist and/or post etch residues from a substrate. The photoresist and post etch residues are removed from the substrate by exposure to an oxygen free plasma. The oxygen free plasma is generated by exposing a plasma gas composition to a microwave source. A preferred plasma gas composition comprises a mixture of a hydrogen bearing gas and a fluorine bearing gas.

[0013] The inventive method includes placing at least one substrate having photoresist and/or post etch resi-

dues thereon into a plasma reaction chamber. A reactive species is formed by generating a plasma in the absence of oxygen wherein a gas for generating the plasma comprises a hydrogen bearing gas and a fluorine bearing gas. The reactive species generated by the mixture removes the photoresist by reacting to form volatile products. The post etch residues are removed by volatilization in the reaction chamber or by weakening adhesion to the substrate or by becoming water soluble.

The residues not volatilized are subsequently removed in a deionized water rinse step. The stripping process continues until the volatile reaction products from the reaction between the photoresist and/or post etch residues are no longer evolved or the photoresist and/or etch residues are rendered water removable.

[0014] The fluorine bearing gas includes those compounds that generate a fluorine reactive species when excited by the plasma. Preferably, the fluorine bearing gas is selected from the group consisting of  $C_xH_yF_z$  wherein x ranges from 1 to 4, y ranges from 0 to 9 and z ranges from 1 to 10,  $NF_3$ ,  $F_2$ , and  $SF_6$ . More preferably, the fluorine compound is  $CF_4$  or  $CHF_3$ .

[0015] The hydrogen bearing gas is selected from the group consisting of a hydrocarbon, hydrofluorocarbons, hydrogen gas or a hydrogen gas mixture. The hydrocarbon may be unsubstituted or may be partially substituted with a halogen such as bromine, chlorine or fluorine, or with oxygen, nitrogen, hydroxyl and amine groups. Preferably, the hydrocarbon has at least one hydrogen and has from one to twelve carbon atoms. Examples of suitable hydrogen bearing gases include methane, ethane, and propane. The hydrogen gas mixture is preferably a mixture of hydrogen gas and an inert gas such as nitrogen, argon, helium, and neon. Preferably, the hydrogen gas mixture is a so-called forming gas which comprises a mixture of the hydrogen gas with the nitrogen gas. For a non-load locked plasma chamber configuration, the hydrogen gas ranges in an amount from about 3 percent to about 5 percent by volume of the forming gas for safety considerations.

[0016] In a particularly preferred embodiment, the plasma gas comprises a mixture of a forming gas and a carbon tetrafluoride gas. The preferred forming gas comprises a mixture of a hydrogen gas and a nitrogen gas wherein the hydrogen gas ranges in an amount from about 3 percent to about 5 percent by volume of the forming gas. The carbon tetrafluoride gas is less than about 10 percent by volume of the total plasma gas. The substrates to be stripped by the plasma are preferably heated from about 80°C to about 350°C to accelerate the reaction time and maximize throughput. For organic low k materials the wafers are preferably heated from about 80°C to about 180°C. The plasma produces fluorine and hydrogen reactive species that are electrically neutral and charged particles thereof. The charged particles are selectively removed prior to reaching the reaction chamber. The neutral species of the plasma reacts with the photoresist and the post etch residues to

for transfer of images to an underlying substrate. The present invention is generally applicable to stripping those photoresists used in g-line, i-line, DUV, 193nm, and 157nm applications. This includes, but is not limited to novolaks, polyvinylphenols, acrylates, and cyclic olefins. Other suitable photoresist formulations will be apparent to those skilled in the art in view of this disclosure. The photoresist may be positive acting or negative acting depending on the photoresist chemistries and developers chosen.

[0025] Referring now to FIG. 1 (A-I), there is depicted a dual damascene process flow commonly used for manufacture of integrated circuits having copper interconnects and low k dielectric layers. The illustrated damascene process is exemplary only. It is understood that a variety of processes can be used to integrate copper and low k dielectrics into the integrated circuit and are generally known by those skilled in the art.

[0026] The damascene process is shown occurring on an underlying first metal layer generally designated 10 having a completed metal interconnect and dielectric layer. The first step in the fabrication of each copper interconnect level is deposition of a thin layer of silicon nitride 12 as shown in Figure 1A. The nitride layer acts as a barrier against diffusion of copper between metal levels and also serves as an etch stop in a dielectric etch process. In Figure 1B, deposition of a thick low k dielectric layer 14 immediately follows deposition of the nitride etch stop layer. The low k material may have a thin layer of oxide on an upper surface. The dielectric layer is patterned by conventional photo-lithographic techniques using a photoresist 16 as a masking material to form the vias as shown in Figure 1C. The photoresist is coated onto the low k dielectric layer, patterned by exposure to activating energy, and subsequently developed to form a relief image. In Figure 1D, the relief image is then partially etched into the dielectric layer using conventional etching techniques known to those skilled in the art. The photo-lithographic process is repeated to form a trench layer and subsequently etched as shown in Figures 1E and 1F. As shown in Figures 1G through 1I, a copper metal deposition process is used to fill the spaces left by the etching and stripping processes to form the second metal layer. Current copper deposition techniques require the deposition of a barrier layer that also acts as a seed layer 17 for subsequent copper deposition as shown in Figure 1G. After the copper 18 has been deposited the wafer surface is then planarized typically by a chemical and mechanical polishing step. The processes are then repeated and the integrated circuit or the like is formed.

[0027] After each etching step, any photoresist and/or post etch residues remaining needs to be removed by stripping so that it does not interfere with any subsequent processing. The inventive stripping process for removing photoresist and/or post etch residues comprises generating an oxygen free plasma from a gas composition comprising a hydrogen bearing gas and a fluorine

bearing gas by exposing the gas composition to an energy source capable of forming a plasma of the gas. The oxygen free plasma gas generates reactive species that selectively react with any photoresist and/or post etch residues remaining after the etching step to form a volatile compound. After stripping, the substrate is sometimes rinsed with deionized water to remove any remaining residues. The particular components of the oxygen free plasma gas are selected by their ability to form a gas and a plasma at plasma forming conditions. Preferably, the components are combined and added to the plasma asher as a gas. The oxygen free plasma gas reacts with carbon and other atoms in the photoresist compounds and post etch residues to form volatile compounds at conditions present in a plasma reaction chamber. Moreover, the oxygen free plasma reacts with those traditionally hard to remove post etch residues that contain silicon embedded in the residue.

[0028] The fluorine bearing compounds used generate sufficient reactive species to increase the selectivity of the photoresist strip rate to the dielectric etch rates on a substrate having photoresist and a dielectric layer underlying the photoresist layer. Preferred fluorine bearing compounds include those compounds that generate a fluorine reactive species when excited by the plasma. Preferably, the fluorine bearing gas is selected from the group consisting of a compound having the formula  $C_xH_yF_z$  wherein x ranges from 1 to 4, y ranges from 0 to 9 and z ranges from 1 to 10,  $NF_3$ ,  $F_2$ , and  $SF_6$ . Other fluorine bearing compounds will be apparent to one of ordinary skill in the art in view of this disclosure. More preferably, the fluorine compound is  $CF_4$  or  $CHF_3$ .

[0029] The hydrogen bearing compounds include those compounds that contain hydrogen, for example, hydrocarbons, hydrofluorocarbons, hydrogen gas or hydrogen gas mixtures. The hydrogen bearing compounds used are ones that generate sufficient reactive species to increase selectivity of the stripping process. Preferably, the hydrogen bearing compound is a non-flammable hydrogen gas mixture with an inert gas such as nitrogen.

[0030] Preferred hydrogen precursor gases are those that exist in a gaseous state and release hydrogen to form reactive hydrogen species such as free radical or hydrogen ions under plasma forming conditions. The gas may be a hydrocarbon that is unsubstituted or may be partially substituted with a halogen such as bromine, chlorine or fluorine, or with oxygen, nitrogen, hydroxyl and amine groups. Preferably, the hydrocarbon has at least one hydrogen and from one to twelve carbon atoms, and more preferably has from three to ten carbon atoms. Examples of suitable hydrogen bearing gases include methane, ethane, ammonia and propane.

[0031] Preferred hydrogen gas mixtures are those gases that contain hydrogen gas and an inert gas. Examples of the inert gas include argon, nitrogen, neon, helium or the like. Especially preferred hydrogen gas mixtures are so-called forming gases which consist es-

may be of the type disclosed in U.S. Patent No. 5,498,308, which is incorporated herein by reference. Air seals/directional feeders 50 and 52 are provided for admitting cooling air and feeding it to the space between the concentric tubes. Air seals/directional feeder 54 is shown at the outlet end and a fourth such unit is present but is not seen.

[0041] Magnetron 56 provides microwave power which is fed through coupler 58 to a waveguide supplying TE<sub>10</sub> mode, having mutually perpendicular sections 60 and 62. The length of waveguide section 62 is adjustable with moveable plunger 64. The bottom plate of waveguide section 62 is iris plate 66, which couples microwave energy into partitioned microwave structure 24, through which the plasma tube 32 extends; thus a plasma is excited in the gas flowing through the plasma tube.

[0042] Referring again to FIG. 3, it is seen that end cap 70 abuts microwave trap 48, and fitting 74 having a central orifice for admitting gas to the plasma tube extends into the end cap. The gas supply is regulated by an external flow box (not shown).

[0043] The plasma tube is supported at this end by □□ ring 72 in the end cap. The outer tube 34 is supported at its ends by abutment against microwave traps 46 and 48. Spacer 76 is present to provide the proper spacing in relation to the process chamber. The other end of the plasma tube is located in end member 78, and has an orifice 80 for emitting gas into the process chamber.

[0044] The plasma reaction chamber 22 includes wafer support pins 90 and 92, which support wafer 98, to be processed. A chuck (not shown) may alternatively be used. Heating may be accomplished by an array of tungsten halogen lamps (not shown) positioned below the wafer. Preferably, the substrate is heated from about 80°C to about 350°C during ashing. More preferably, the substrate is stepwise heated by incrementally increasing the temperature. Heating has been found to increase the reaction rate of the plasma with the photoresist and/or post etch residues and consequently, increase throughput. One or more baffle plates may be present above the wafer to promote even distribution of the plasma to the surface. Additionally, the reaction chamber may include a monochromator (not shown) The monochromator optically detects an emission peak having a particular wavelength range that corresponds to the reaction product between the plasma and the photoresist.

[0045] Referring to FIG. 4, an exterior view of the device is shown. The reference numerals in Figure 4 correspond to those which are used in the other Figures.

[0046] Preferably, the microwave enclosure 24 is dimensioned to support the rectangular TM<sub>110</sub> mode and the enclosure 24 may have a square cross section. The dimensions of the cross sections are such that the TM<sub>110</sub> mode is resonant. The length of each section is less than  $\lambda_g/2$  where  $\lambda_g$  is the guide length within the cavity of the TE<sub>104</sub> mode.

[0047] In operation, the semiconductor wafer 98 with

photoresist and/or post etch residues thereon is placed into the reaction chamber 22 on wafer support pins 90 and 92. The wafer is preferably heated to accelerate the reaction of the photoresist and/or post etch residues with the plasma. The pressure within the reaction chamber is reduced. Preferably the pressure is maintained between about 1 torr to about 5 torr. An excitable gas mixture of the hydrogen bearing gas and the fluorine bearing gas is fed into plasma tube 32 of the plasma generating chamber 21 via a gas inlet 23 (as shown in Figure 5). The fluorine bearing gas is preferably less than 10 percent of the total gas composition. Each section 26, 28, 30 is fed with microwave energy to excite a plasma in the plasma tube, which plasma is comprised of electrically neutral and charged particles. The charged particles are selectively removed prior to the plasma entering the reaction chamber. It is believed that the excited or energetic atoms of fluorine (atomic fluorine) and hydrogen (atomic hydrogen) are fed into the reaction chamber and react with the photoresist and/or post etch residue. A principal reaction product, methane gas, evolves and is monitored optically by the monochromator. The methane gas is continuously swept away by a gas sweep within the reaction chamber. The monochromator detects the emission peak of methane. Once the emission peak reaches a minimum the removal of photoresist and/or post etch residues is complete and the plasma is turned off. Alternatively, the plasma may be run for a predetermined time. This has been found to be particularly useful for removing post etch residues from the substrate wherein the photoresist remaining after etch is minimal. It has been found that the emission peak is not be easily detected if a sufficient quantity of photoresist is not present. It is believed that a detectable emission peak is primarily derived from the reaction between the plasma and the photoresist. A deionized water rinse is then used to remove any remaining residue on the stripped wafer. The vacuum is then released and the processed wafers are removed from the reaction chamber.

#### Example 1.

[0048] In the following example, a DUV photoresist was coated onto multiple hexamethyldimethylsilane treated silicon wafers at 3000 rpm. The photoresist is available under the trade name UV5-1.0 and commercially available from Shipley Company. After softbaking each wafer for 45 seconds at 130°C on a vacuum hotplate a tack free photoresist film was obtained having a thickness of about 10,000 angstroms. The photoresist film was then exposed to microwave plasma using a Fusion Gemini ES Plasma Asher available from Eaton Corporation. The plasma chamber power was set at 1800W with a chamber pressure of 1.5 torr. The wafers were divided into two sets of three wafers. One set of wafers were individually exposed to a plasma generated from forming gas with a gas flow rate of 3500 sccm. The other

orine bearing gas is selected from the group consisting of a compound having a formula  $C_xH_yF_z$  wherein x ranges from 1 to 4, y ranges from 0 to 9 and z ranges from 1 to 10,  $NF_3$ ,  $F_2$ , and  $SF_6$ .

3. The method according to claim 1 wherein said hydrogen bearing gas is selected from the group consisting of a hydrocarbon, hydrofluorocarbon, hydrogen gas and a hydrogen gas mixture.
4. The method according to claim 3 wherein said hydrogen gas mixture comprises a forming gas comprising nitrogen and hydrogen gas wherein said hydrogen gas is in an amount from about 3 percent to about 5 percent by volume of the forming gas.
5. The method according to claim 1 wherein said substrate 98 comprises an insulating layer 12.
6. The method according to claim 1 wherein said substrate 98 comprises a material having a low k dielectric constant.
7. The method according to claim 6 wherein said low k dielectric is selected from porous materials and doped oxide materials.
8. The method according to claim 6 further comprising heating said substrate 98 from a range of about 80°C to about 350°C.
9. The method according to claim 7 wherein said low k dielectric is organic.
10. The method according to claim 9 further comprising heating said substrate 98 from a range of about 80°C to about 180°C.
11. The method according to claim 6 wherein a dielectric constant of said low k dielectric remains substantially constant before and after removing said photoresist 16 and said post etch residues.
12. The method according to claim 1 comprising reacting said reactive species of said plasma with said photoresist 16 and said post etch residues to produce volatile alkanes.
13. The method according to claim 12 wherein said volatile alkanes comprise methane gas.
14. The method according to claim 1 wherein said fluorine bearing gas is less than about 10 percent by volume of the total plasma gas.
15. The method according to claim 1 comprising generating said plasma by microwave to produce electrically neutral and charged particles, removing said

charged particles from said plasma and reacting said electrically neutral particles with said photoresist 16 and said post etch residues.

- 5 16. The method according to claim 1 wherein an etching selectivity of said plasma between the photoresist 16 and/or post etch residues, and the substrate 98 is greater than about 10 to 1.
- 10 17. An ashing method for stripping photoresist 16 and/or post etch residues from a semiconductor wafer 98; said method comprising:
  - 15 a. placing said semiconductor wafer 98 having said photoresist 16 and said post etch residues into a reaction chamber 22;
  - b. generating a plasma by subjecting a gas consisting essentially of a hydrogen bearing gas and a fluorine bearing gas to microwaves wherein said plasma contains both electrically neutral species and charged particles;
  - c. removing said charged particles from said plasma; and
  - 25 d. ashing the organic residue on said semiconductor wafer by exposing said wafer 98 having the photoresist 16 and the organic residue thereon to said electrically neutral species.
- 30 18. The ashing method of claim 17 wherein said gas plasma is created in a plasma generating chamber 21 adjacent said reaction chamber 22, and said electrically neutral species are caused to flow out of said plasma generating chamber 21 and into said reaction chamber 22 through at least one baffle plate between the plasma generating chamber 21 and the reaction chamber 22.
- 35 19. The ashing method of claim 18 wherein said substrate 98 is placed within said reaction chamber 22 such that the organic residue reacts only with said electrically neutral species flowing through said baffles during ashing.
- 40 20. The ashing method of claim 17 further comprising heating said wafer 98 from about 80°C to about 350°C.
- 45 21. The ashing method of claim 17 wherein said fluorine bearing gas is selected from the group consisting of a compound having the formula  $C_xH_yF_z$  wherein x ranges from 1 to 4, y ranges from 0 to 9 and z ranges from 1 to 10,  $NF_3$ ,  $F_2$ , and  $SF_6$ .
- 50 22. The method according to claim 17 wherein said hydrogen bearing gas is selected from the group consisting of a hydrogen, hydrocarbon, hydrofluorocarbon, and a hydrogen gas mixture.
- 55

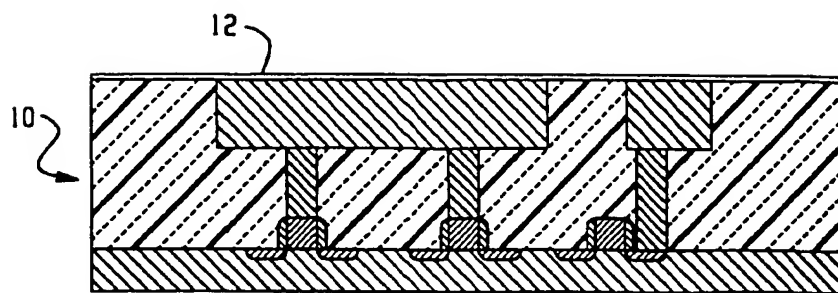


Fig. 1A

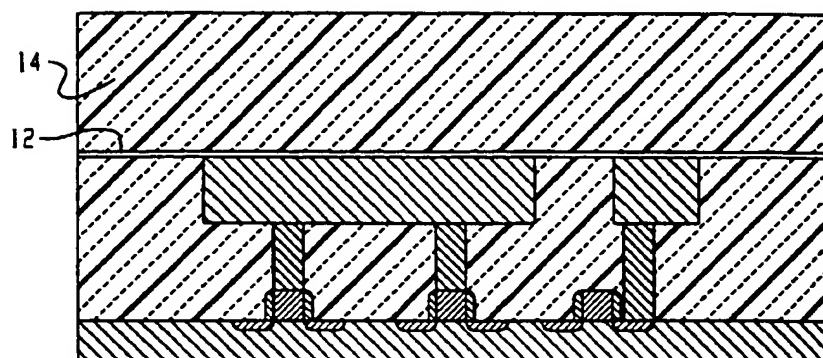


Fig. 1B

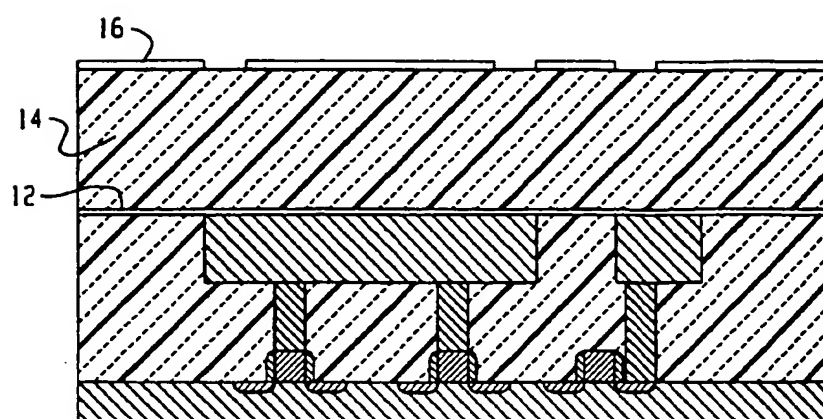


Fig. 1C

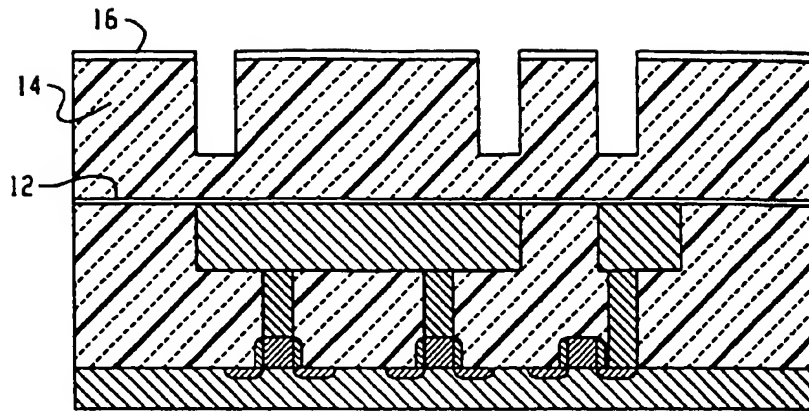


Fig. 1D

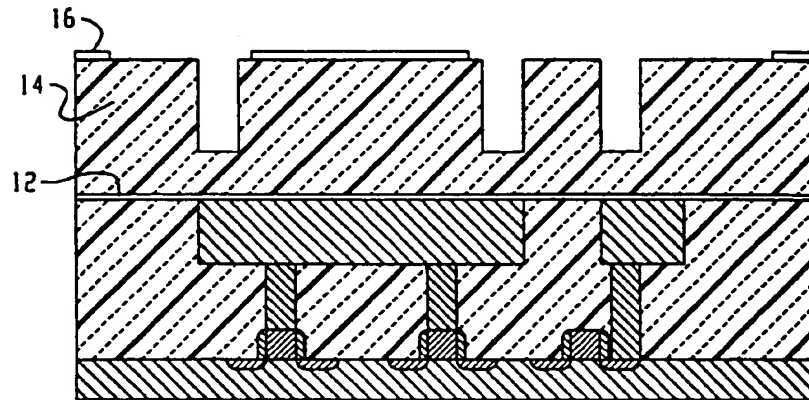


Fig. 1E

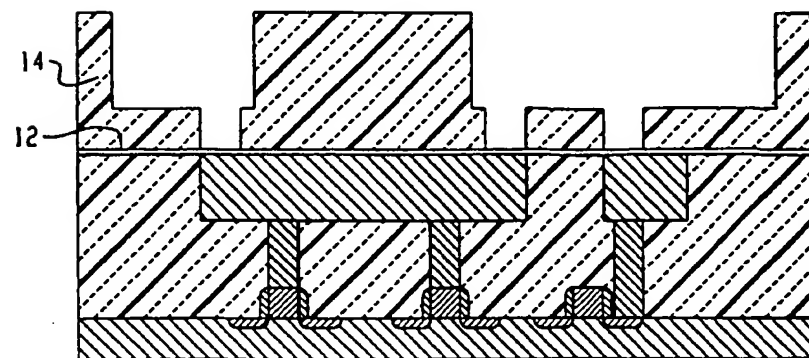


Fig. 1F



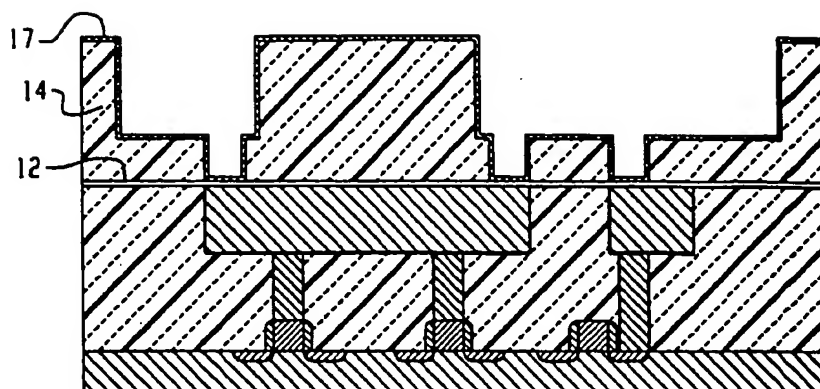


Fig. 1G

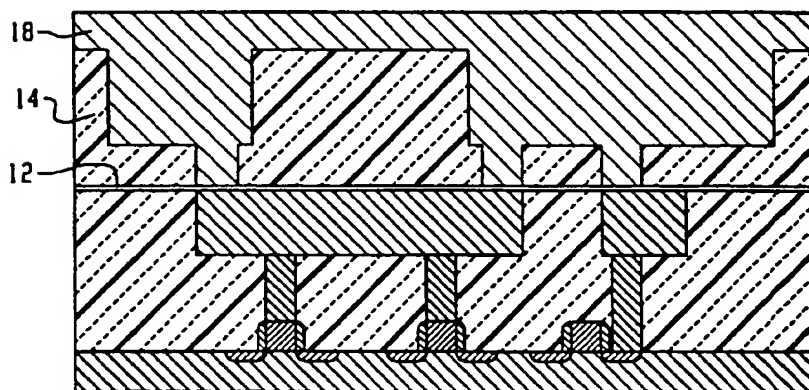


Fig. 1H

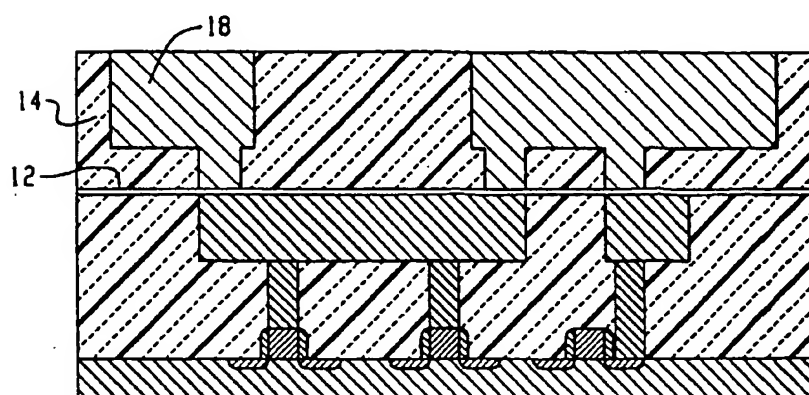
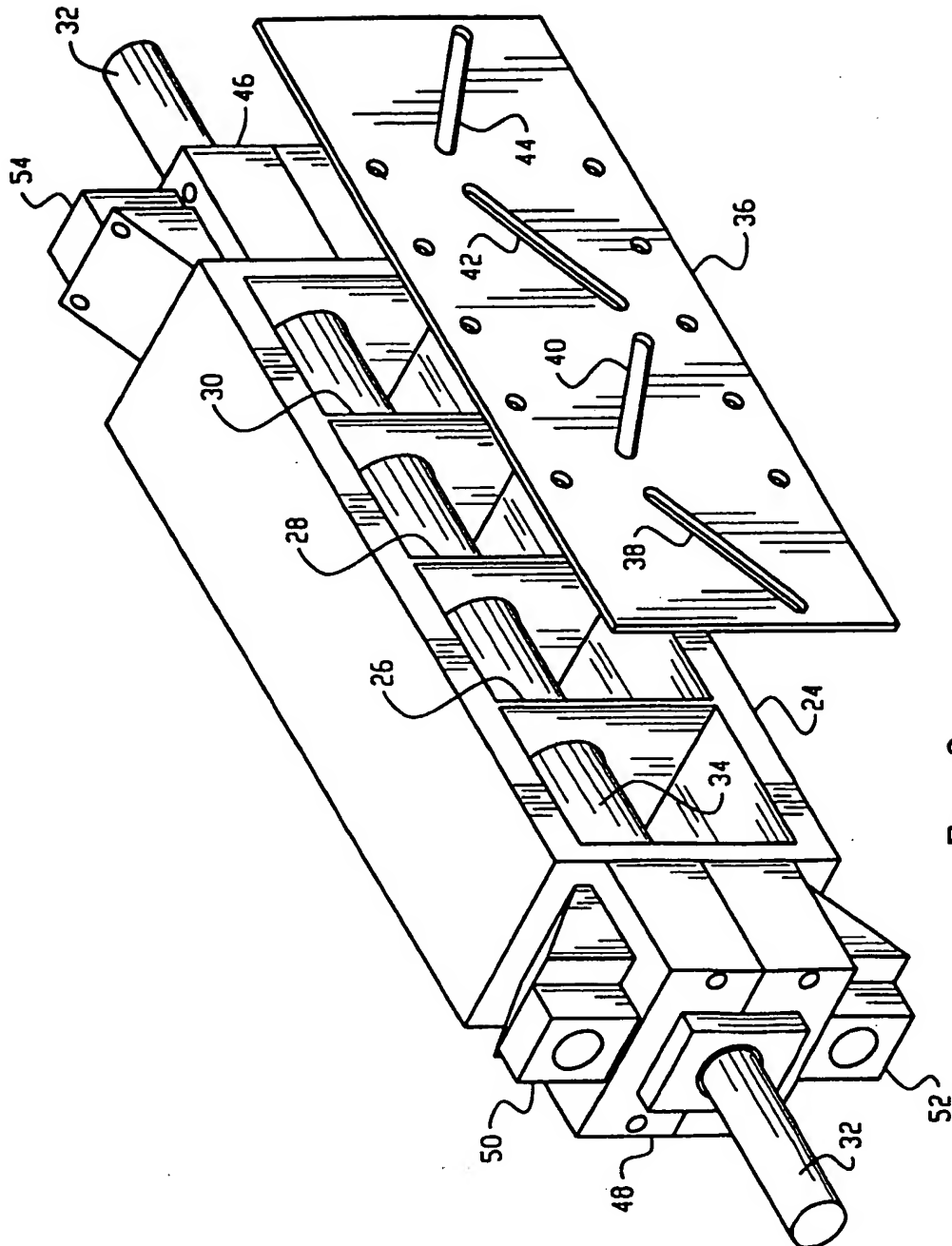
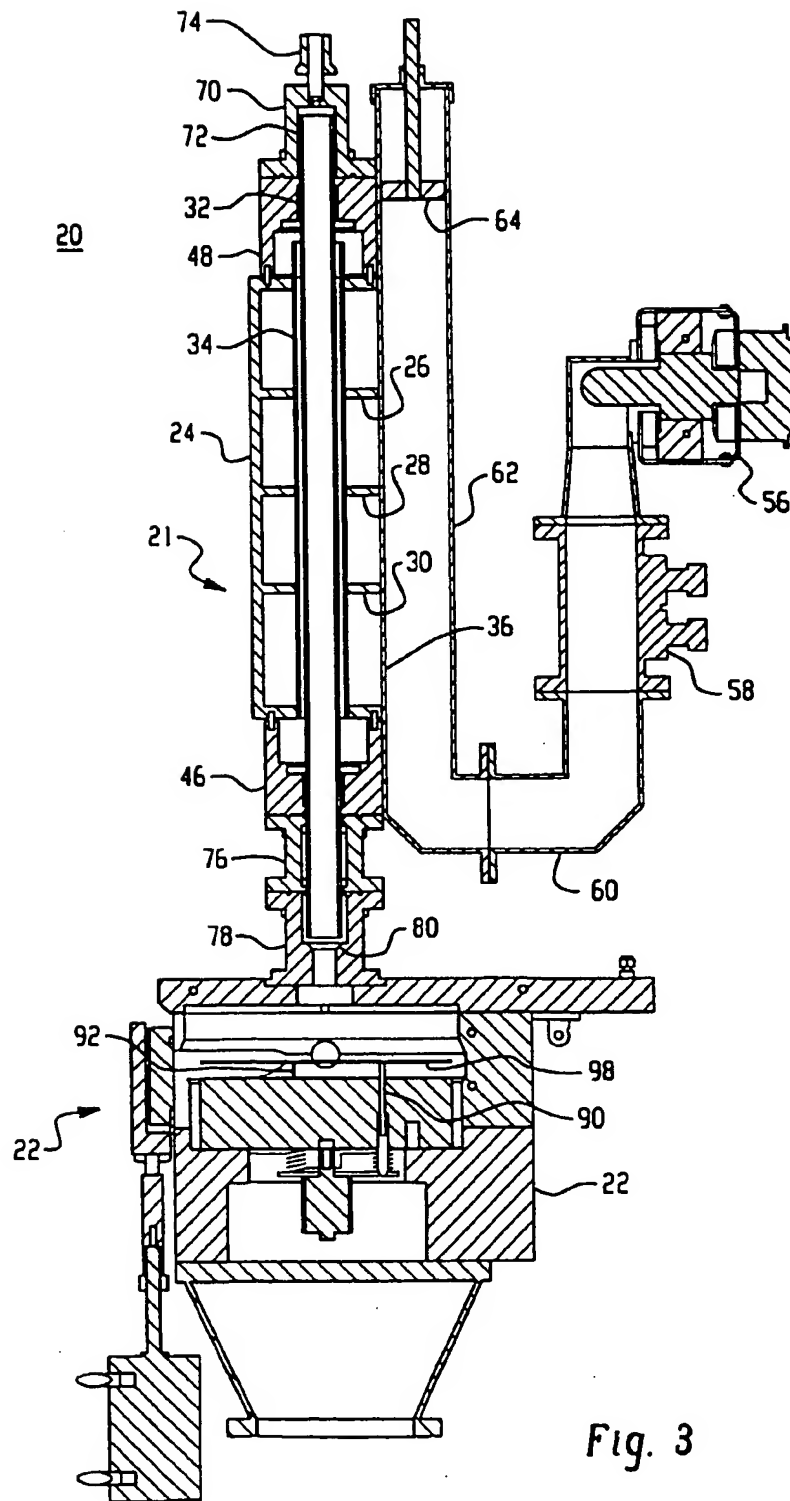


Fig. 1I



**Fig. 2**



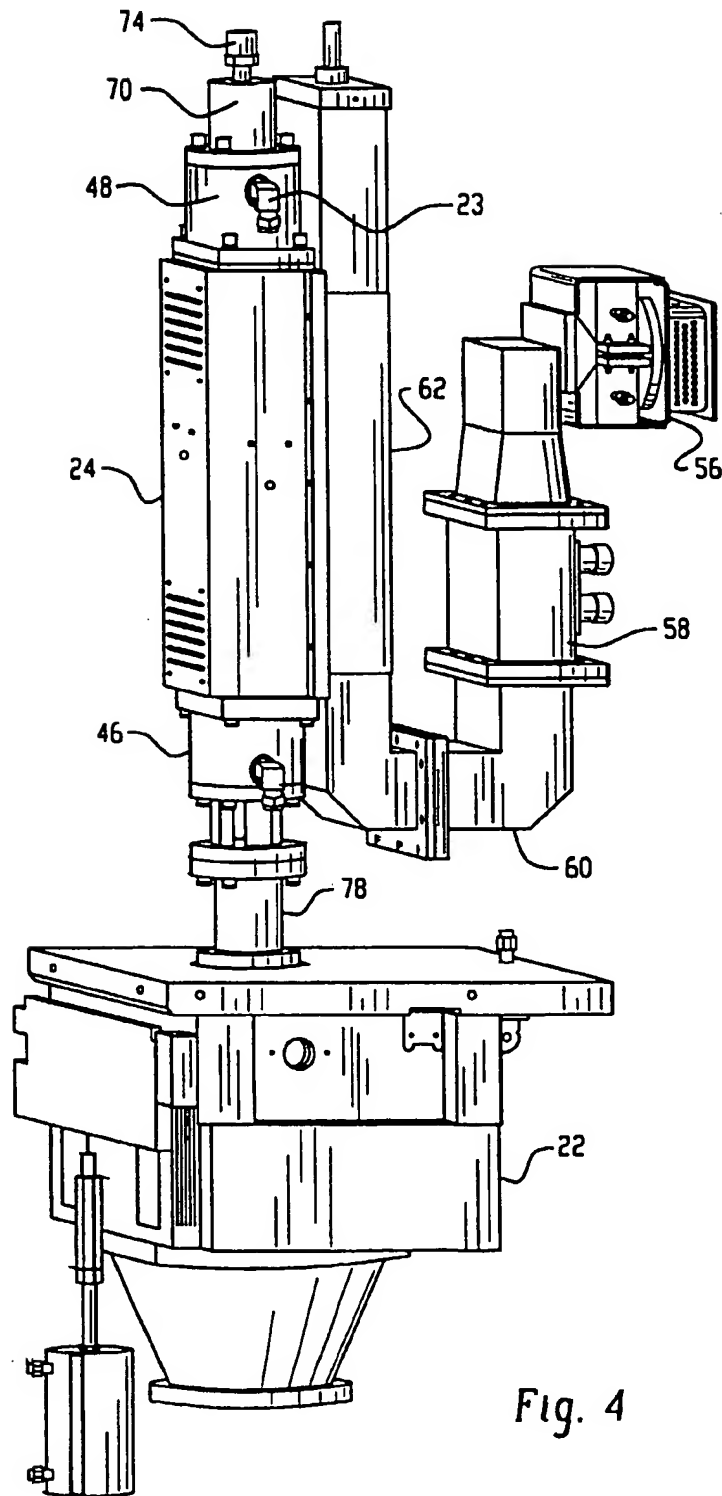


Fig. 4

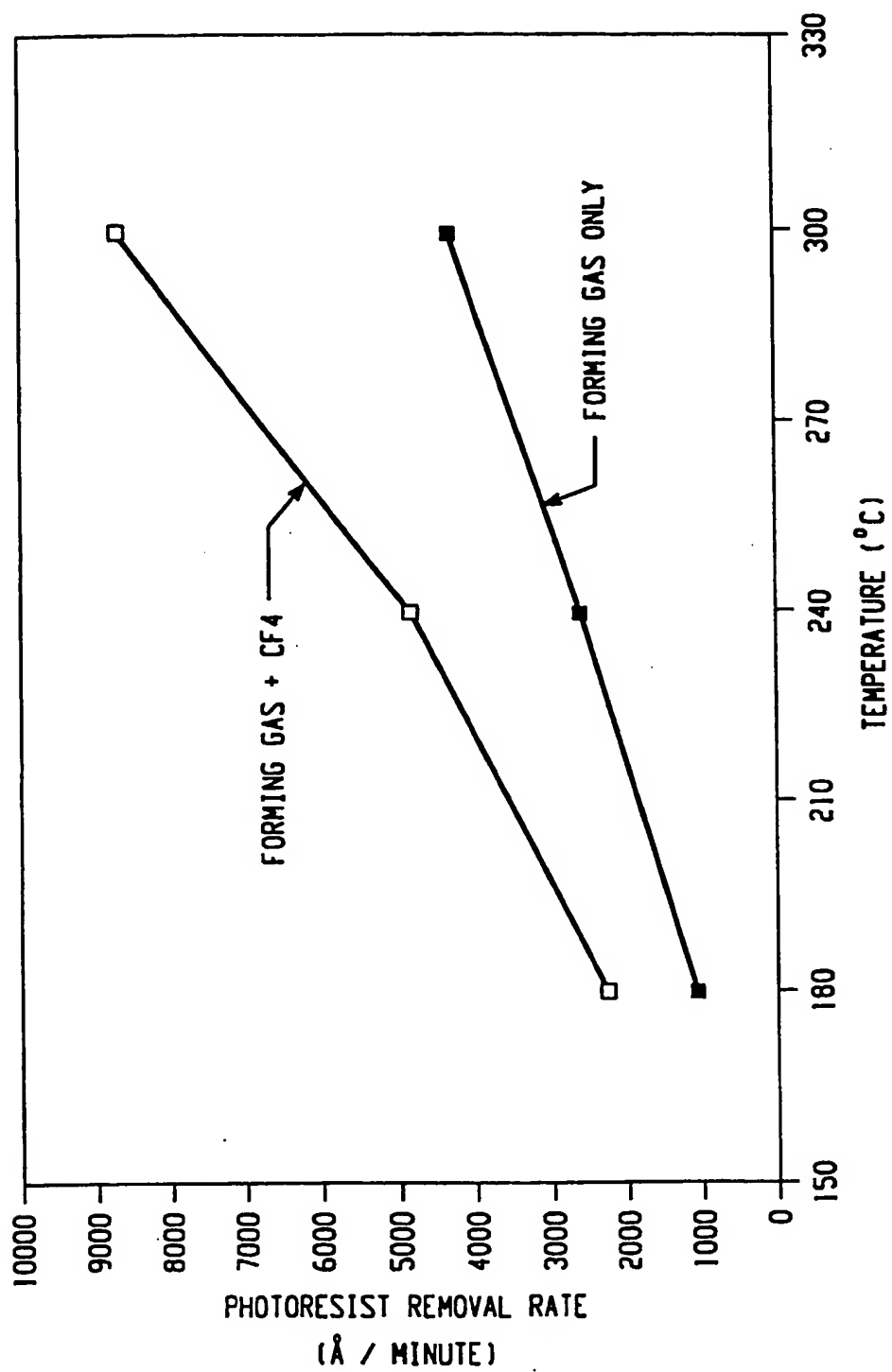


Fig. 5